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REPORT NO. 345/6

TINLESS SOLDER INVESTIGATION

INDEXED

By

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June 24, 1937

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Report No. 345/6
Watertown Arsenal

June 24, 1937

TINLESS SOLDER INVESTIGATION

Conclusions

1. A lead-cadmium-zinc mixture of 79-82% Pb, 17-20% Cd, 1-2% Zn, makes a solder equal or superior (with some materials) to half and half lead-tin solder in its tensile strength of soldered lap joints.

2. The above mixture is the eutectic mixture of lead and cadmium to which has been added 1-2% zinc.

3. By soldering uncoated plates of bright annealed sheet iron and sheet brass with this mixture, the tensile strength in shear is far superior to half and half lead-tin solder.

4. By soldering coated thin (.015") plates of tin-plate, terne-plate and galvanized iron with this mixture, the tensile strength in shear is only slightly greater than soldering with half and half lead-tin solder.

5. By soldering coated thick (.035") plates of tin-plate, terne-plate and galvanized iron with this mixture, the tensile strength in shear in considerably greater than soldering with half and half lead-tin solder.

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6. The soldering copper temperature must be at least 100°C higher (about 400°C) when soldering with this mixture than when soldering with half and half lead-tin solder. Unless this is taken into account, it is a disadvantage because incomplete soldered joints will result, thereby giving poor, erratic results.

7. The tensile strengths of soldered lap joints are so good that other physical and corrosion properties should be studied.

8. At present the price* of metallic cadmium is so high that this mixture probably could not compete commercially with half and half lead-tin solder, except where greater strengths of soldered lap joints are required.

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*Market quotation as given in Ind. & Eng. Chem., June 1937, Cadmium $1.20/lb; Tin $.54 5/8 per lb; Lead $.06/lb; Zinc $.075/lb.

Experimental

This report is a continuation of the investigation reported in the Experimental Report No. 377A.

Some sixty mixtures had been made of the lead-cadmium eutectic, to which had been added various small amounts of bismuth, zinc and tin. These additions had been made either singly or in combination with the others. A maximum of 10% and a minimum of 1% of any of these elements were used.

Preliminary tests were in many cases erratic, even though the temperature of the soldering copper was thermostatically controlled to within ±10% C. Numerous other factors were kept constant, such as the pressure on the overlapping plates, length of time the solder remained liquid, the temperature of the plate preheating, width of lap, etc. The tests were so erratic that a satisfactory average could not be obtained except by the Method of Least Squares applied to many tests. That was ~~considered~~ a factor which was variable and not sufficiently controlled. Examination of the broken tests revealed that the size of the fillet varied considerably. An experiment using half and half solder with variable fillets showed that the size of the fillet had tremendous effect on the shear strength of the soldered lap joint.

Table I*

A. Plates tinned and excess solder wiped off while still melted. Joint sweated together.

All joints broke in tinsmith's shear when preparing test specimens.

B. Plates tinned, soldered, and top and bottom fillet filed off with a square file.

5500 lbs/in^2	
4800 lbs/in^2	
4800 lbs/in^2	
5000 lbs/in^2	Average 5000 lbs/in^2

C. Plates tinned, soldered, making as small a fillet as possible. Fillet did not cover more than one-half the thickness of .025" plate.

5600 lbs/in^2	
6000 lbs/in^2	
5800 lbs/in^2	
5800 lbs/in^2	Average 5800 lbs/in^2

D. Plates tinned, soldered. Top fillet wiped to a concave fillet. Fillet wet top of upper plate. Bottom fillet filed off.

6300 lbs/in^2	
6700 lbs/in^2	
6200 lbs/in^2	
6200 lbs/in^2	Average 6400 lbs/in^2

Table I* (Cont'd)

E. Plates tinned, soldered. Top fillet convex but just flush with upper plate. Bottom fillet filed off.

7300 lbs/in^2

8000 lbs/in^2

8000 lbs/in^2

7500 lbs/in^2 Average 7800 lbs/in^2

F. Plates tinned, soldered. Top fillet convex but covers completely top plate. Bottom fillet filed off.

9300 lbs/in^2

9300 lbs/in^2

9300 lbs/in^2

9700 lbs/in^2

9700 lbs/in^2 Average 9600 lbs/in^2

*The plates used in this test were tin-plate. Tests on bright annealed, terne-plate, brass and galvanized showed a similar trend.

In the following tests, the bottom fillets were filed off, the top fillet filed flush with the top plate, so as to keep a fillet size and shape as nearly constant as possible.

The results of the fillet tests explained the erratic results and practically nullified all the previous tests. However, two generalizations could be drawn: (1) mixture containing tin and bismuth gave lower results than had the alloys with zinc; (2) the mixtures containing tin and bismuth fouled the soldering copper much faster than those containing zinc. It was thought that the oxidized alloy was getting into the joint in quantities too large to be fluxed by the soldering flux. Examination of the worst tests confirmed this.

Inasmuch as some of the solders seem to oxidize readily, and moreover, retesting all the mixtures with the now standardized fillet would be very expensive, it was decided to eliminate the worst offenders as regards rapidity of oxidation.

After some experimentation, the following method of classification was adopted. A thermally controlled electric melting pot was nearly filled with molten lead on which floated a large cast iron thick plate. In this plate holes were drilled partway through. Over these holes, inverted porcelain crucible covers were placed. A thermocouple, connected with the Leeds and Northrup controlling potentiometer, was placed in a hole drilled in the center of the cast iron plate.

In the crucible covers were placed the solder mixtures to be tested. The area exposed to the air was large compared to the volume of solder used. (The covers were about 45 mm. in diameter and about 3 mm. deep. They held about 60 grams of melted solder.)

The solders were weighed before starting the test and heated to the soldering temperature of 400°C. They were examined visually frequently during the first hour, and then hourly for eight hours. If the mixtures were not too badly oxidized after eight hours, the heating was continued for twenty-four hours. Then the mixtures were cooled by removing the covers and weighed when cold. They were replaced on the hot plate and heated continuously for another twenty-four hours, cooled and reweighed. The gain in weight indicated their tendency to oxidize. (Note the oxide film was not disturbed any more than could be helped during the test.)

Inasmuch as the weights of the solders and the diameters of the covers were very nearly the same, the total gain in weight, not the gain in weight per square centimeter, was used to evaluate the oxidizing tendency.

Table II gives the results of this evaluation. All solders containing tin oxidized very rapidly. This oxide was loosely granular and the alloys were practically 100% oxidized in one-half to two hours. The mixtures containing tin alone oxidized the most rapidly, those containing tin and zinc the least rapidly. By experimentation it was found that cadmium-tin part of the mixture was the offender.

The mixtures containing tin will not appear in the table below.

Table II

Spec.	Composition				Gain in Weight (grams)	
No.	Pb	Cd	Zn	Bi	24 hours	48 hours
1/2 & 1/2					.0006	.0007
26	81.7	17.3	1.0		.0008	.0019
4	78.8	19.7	1.5		.0002	.0008
27	80.7	17.3	2.0		.0003	.0014
2	90.0	6.0	2.0		.0000	.0012
28	79.2	16.8	4.0		.0003	.0005
29	81.7	17.3		1.0	.0520	.0528
30	80.7	17.3		2.0	*	*
31	79.2	16.8		4.0	.0353	.0563
12	70.0	20.0		10.0	.0463	.0763

*Crucible of solder #~~28~~ 30 broke during cooling and test was lost.

Table II (Cont'd)

Spec. No.	Composition Pb	Cd	Zn	Bi	Gain in Weight (grams) 24 hours	48 hours
37	79.2	16.8	2.0	2.0	.0024	.0043
38	77.6	16.4	2.0	4.0	.0029	.0050
14	71.6	21.4	2.0	5.0	.0060	.0108
39	74.3	15.7	2.0	8.0	.0032	.0071
15	67.8	20.2	2.0	10.0	.0069	.0117
41	75.9	16.1	4.0	4.0	0000	.0047
42	72.6	15.4	4.0	8.0	.0044	.0103

From the above table it will be noted that the mixtures of lead cadmium and zinc oxidize slowly, e.g., the oxide film protects the underlying liquid. The mixtures containing lead, cadmium and bismuth oxidize fairly rapidly. The mixtures containing lead, cadmium, zinc, and bismuth oxidize more rapidly than those without bismuth, but much less rapidly than those without zinc, and the more the amount of zinc the less is the oxidation. This means that the oxide film caused by the added zinc is continuous and fairly impervious to oxygen.

As a result of this test, all mixtures containing tin and mixtures with bismuth, with less than 4% of zinc, were discontinued, and the mixtures containing bismuth with

4% zinc were viewed with disfavor. This left five mixtures containing only zinc additions and two doubtful ones containing both bismuth and zinc.

Because of the pressure of other work, the study of tinless solders was discontinued for several months.

When this investigation was resumed, the plate stock had rusted or oxidized considerably. The usual method of cleaning was used but very erratic results were obtained. Examination of the fractured joints showed that there were numerous areas that had not been wet by the solder, thereby accounting for the erratic and nonduplicating results.

Inasmuch as several of the plates (tin-plate, terneplate and galvanized iron) had coatings, it was impossible to use emery cloth on them to completely remove the rust or oxidized films without danger of cutting through and removing the coatings. In other words, these three would become virtually bright annealed sheets with probably a little of the coating left here and there.

Various chemicals were tried, such as hydrochloric, nitric, acetic and sulphuric acids, ammonia, sodium hydroxide, etc., both cold and hot, and in various concentrations, with poor results on some of the plates. Finally, the following procedure was adopted with good results, provided the cleaned plates were used within a few hours after treating.

Ordinary zinc chloride soldering flux was heated nearly to boiling. This hot solution was rubbed over the surface of the plate to be soldered. After a few minutes, the surface was clean and bright. The treated plates were then washed with water and quickly dried. The plates were now ready to use. If used in a few hours after this cleaning, the flux put on at the time of soldering was sufficient to take care of the oxide film which formed between the time of cleaning and soldering. This cleaning operation did not seem to cut through the original coatings on the plates. Therefore, the tests were of the solder on these coatings and not of the solder on the sheet iron base material.

The following tables give the results of soldering the plates after the above cleaning, using a 1/8" lap, a soldering temperature of 400°C, a soldering time of thirty seconds with the .015", and sixty seconds with the .035" thick plates. The laps were pressed together while soldering with an effective weight of five pounds. The soldering flux was zinc chloride made by "killing" 1.1 sp. gr. HCl with zinc. The fillets were: top-convex, flush with top plate; bottom-filed off. An example of the variations of the individual tests using the above procedure is given in Table III. Solder - half and half. Material- .015" thick bright annealed plate.

TABLE III

Tensile Strength in Shear lbs/in^2	Mean Deviation lbs/in^2
5500	- 350
6080	+ 230
6080	+ 230
5830	- 20
5830	- 20
6000	+ 150
6080	+ 230
5500	- 350
5500	- 350
5830	- 20
5830	- 20
5745	- 105
6000	+ 150
5830	- 20
6080	+ 230
5500	- 350
5830	- 20
5745	- 105
6080	+ 230
6080	+ 230
Ave. 5850	Ave. ± 170

To give tables of the individual tests for all the solders and the various plates would make a tiresome report to read, so a condensed table showing the averages is given. All of the averages are within an average mean deviation of ± 200 lbs/in^2.

Table IV

.015" Plate Thickness

Material*	1/2 & 1/2	0% Zn	1% Zn	1 1/2% Zn	2% Zn	4% Zn
B.A.	5850	6110	6480	6600	6400	6510
T	6700	6200	6200	6600	6400	6510
Tr	6300	5800	6500	7250	6800	6700
B	6400	6900	6900	6900	6700	6700
G	5100	4800	4600	4900	5300	4900

Table V

.035" Plate Thickness

Material*	1/2 & 1/2	0% Zn	1% Zn	1 1/2% Zn	2% Zn	4% Zn
B.A.	7480	10000	10680	11100	10600	10500
T	7700	8700	7500	8300	6800	7500
Tr	5400	5400	6000	5350	5400	5200
B	6700	10000	10500	10800	10000	10100
G	7140	6400	5600	6110	6120	6000

All values given under the various solders are lbs/in^2.

*B.A. = Bright Anneal Sheet Iron
T = Tin-plate
Tr = Terne-plate
B = Brass (sheet)
G = Galvanized iron

Graphs, Figures 1 - 5 inclusive, show the above data plotted as plate material vs. solder composition. Both light and heavy plate of the same material are plotted on the graphs.

Graphs, Figures 6 - 11 inclusive, show the above data, but plotted so that each solder is plotted against the various materials on the same graph.

Discussion

It will be observed that no one solder is best for all materials. However, the mixture containing 1 1/2% zinc comes nearest to that condition. The uncoated plate joints are very much stronger (especially the heavy plates) when soldered with lead-cadmium-zinc solders than with the standard half and half solder. The coated plate joints (especially the light plates) when soldered with lead-cadmium-zinc solders are about equal to half and half soldered joints. The high temperature required in soldering the lead-cadmium-zinc solders probably oxidizes the coatings more than when half and half solder is used. This may explain why the coated plates do not show such superiority over half and half solders as the uncoated plates do.

The tensile strength of soldered lap joints using the eutectic proportions of lead and cadmium with 1 1/2 - 2% zinc added is equal to (and with the uncoated materials tried, far superior to) the strengths of joints soldered with 50% lead and 50% tin solder, but the soldering operation demands a considerable higher temperature. How these solders will compare in shock and corrosion resistance is unknown and should be investigated.

In spite of the fact that half and half solder has been used for years and by many artisans, few can make soldered lap joints which can be duplicated quantitatively in strength. In order to get reasonable duplication, many conditions governing soldering had to be investigated. Probably there are many more as yet unknown. Among those investigated were: soldering copper temperature, length of time the solder must be kept melted vs. thickness of the plate, thickness of the solder layer between the plates, width of lap, removal of oxide films on old stock, etc.

Sheet zinc was also soldered successfully but in all tests of soldered lap joints, the joints were stronger than the zinc sheet itself (fracture always occurred in the zinc, never in the joint), so the study of soldered lap joints of sheet zinc was discontinued.

Respectfully submitted,

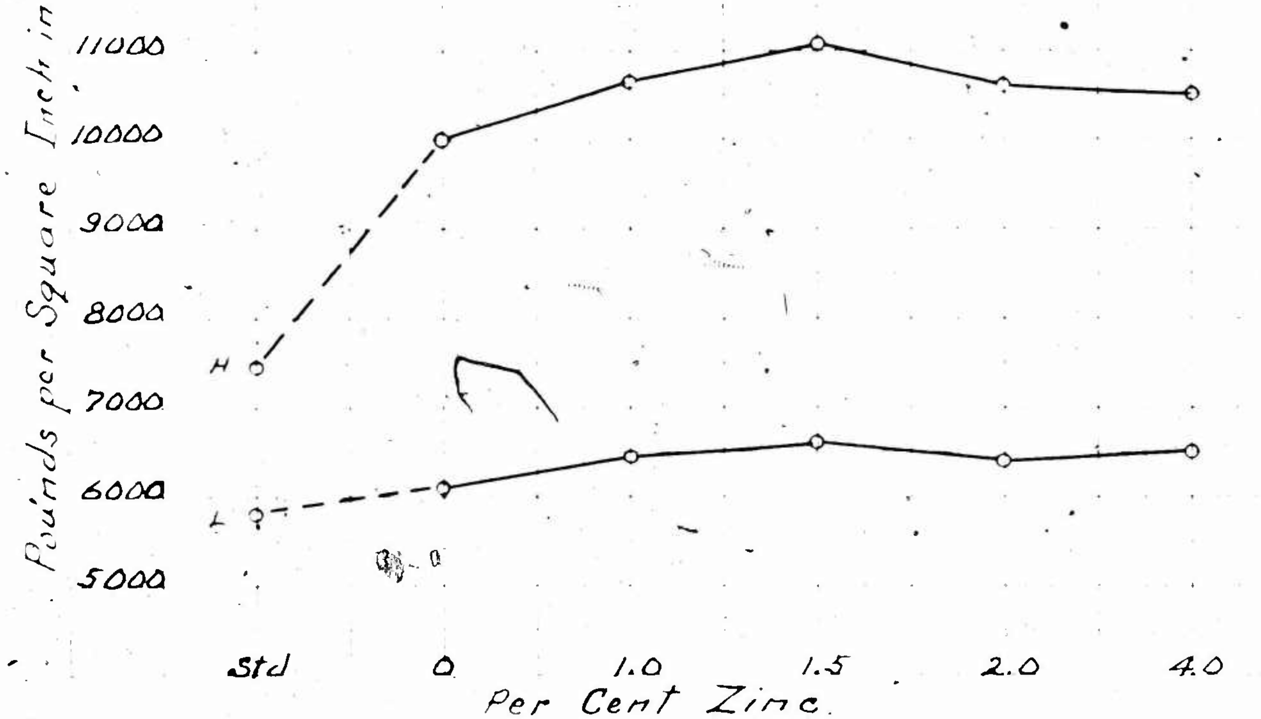
H G Carter

H. G. Carter,
Assoc. Metallurgist.

Tinless Solder.

Bright + Anneal. Plate vs. Composition.

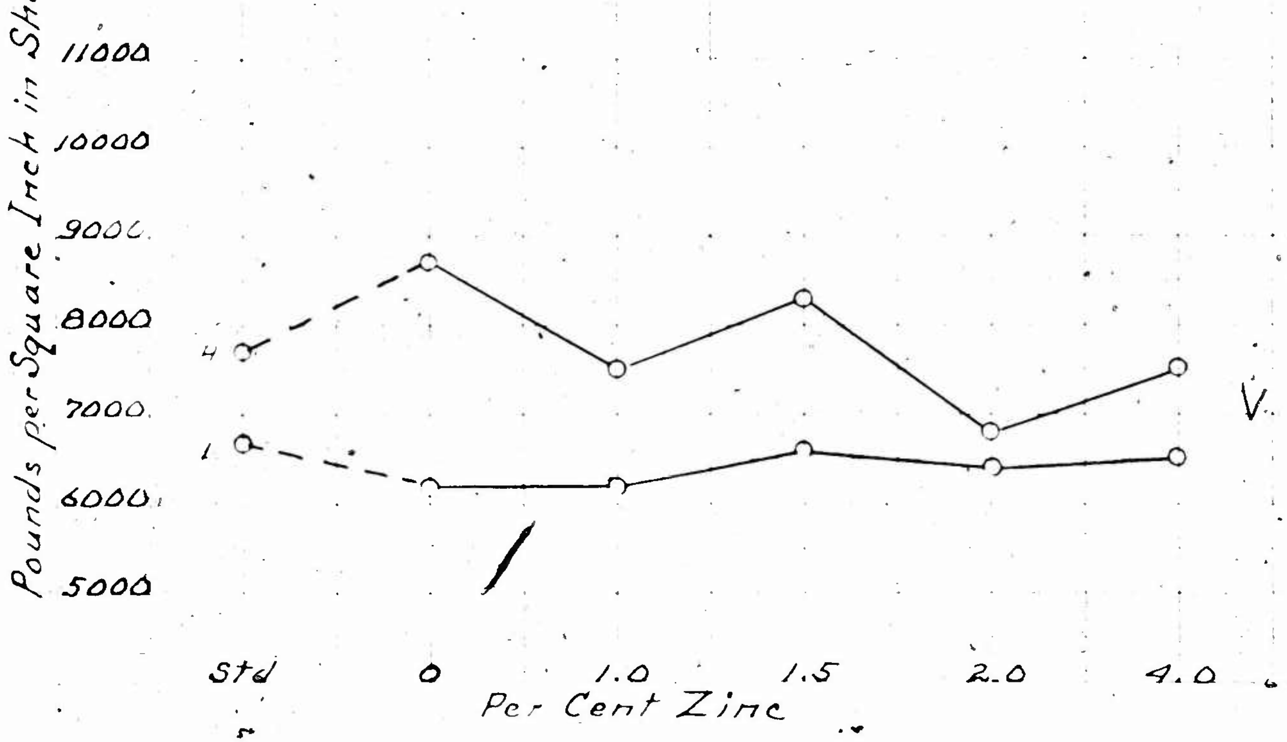
Fig. 1.



Tinless Solder

Tin Plate vs Composition

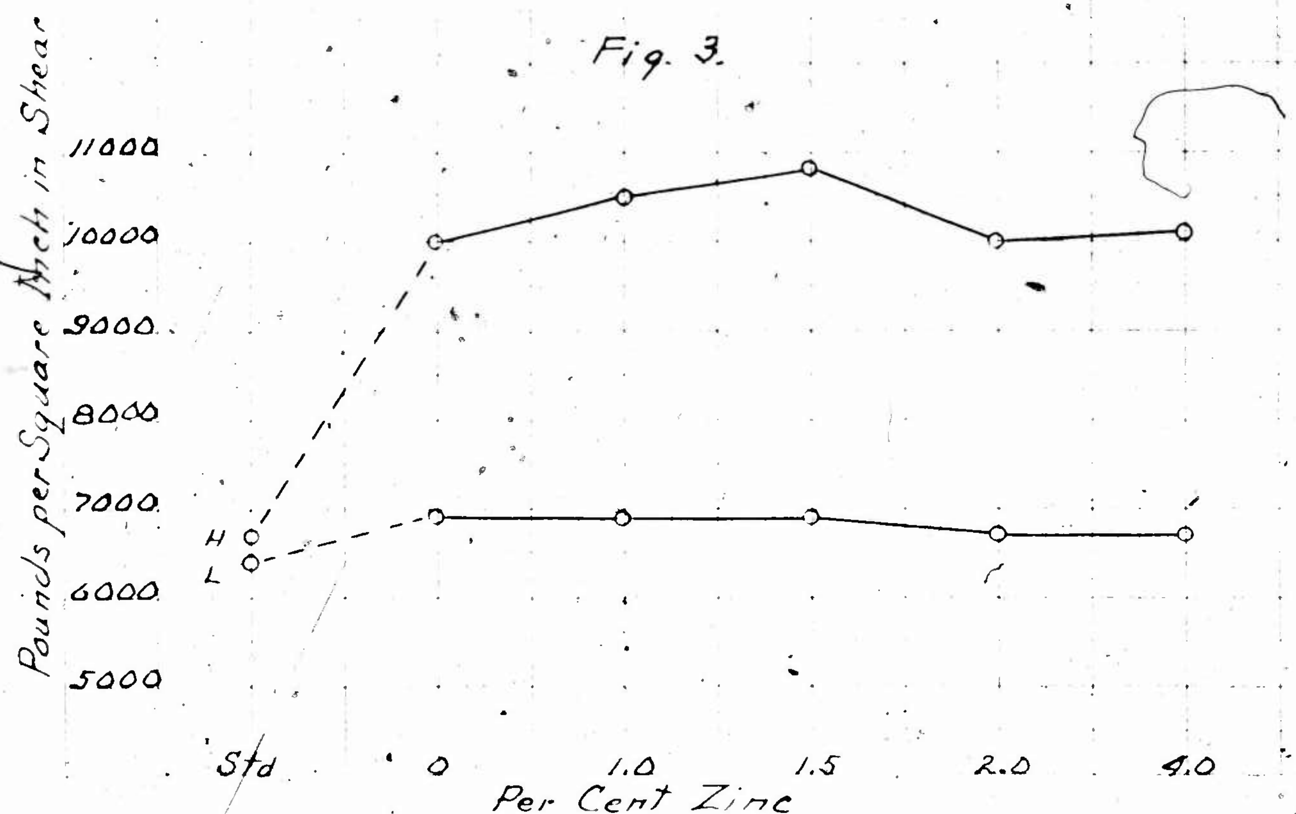
Fig. 2.



Tinless Solder

Brass Plate vs Composition

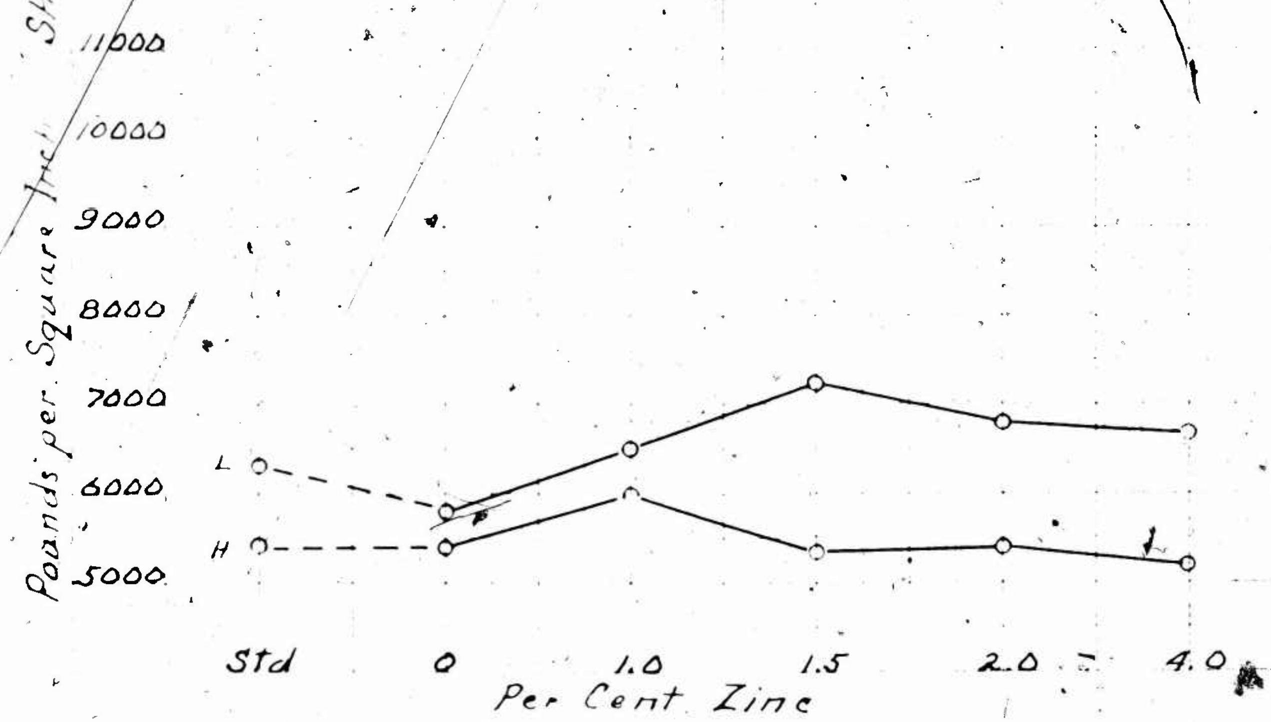
Fig. 3.



Tinless Solder.

Terne Plate. vs. Composition

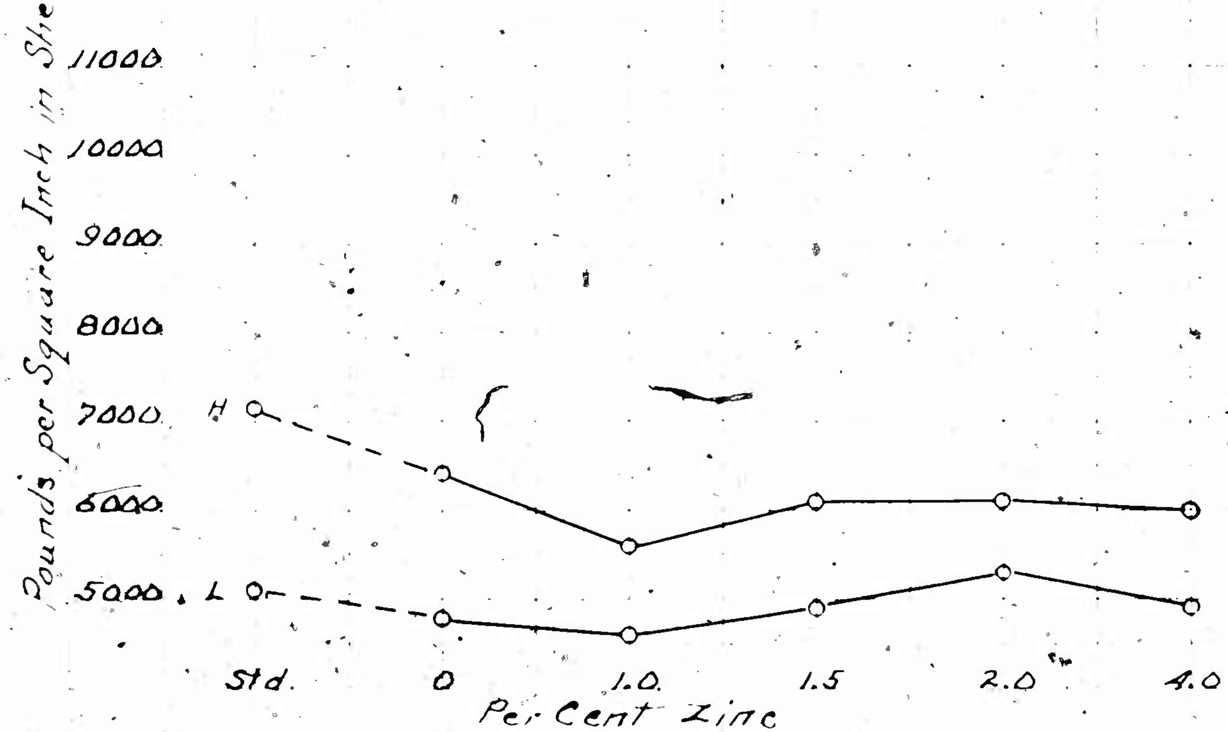
Fig. 4.



Tinless Solder

Galvanized Plate vs Composition

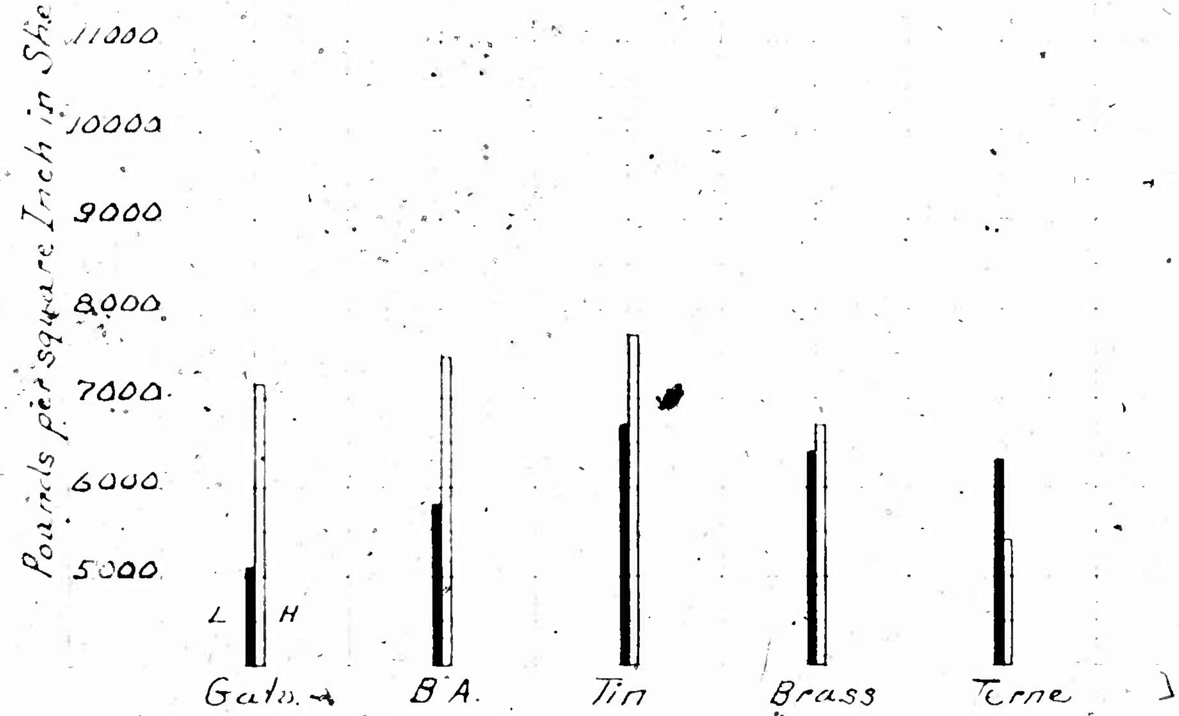
Fig. 5



Tinless Solder

Standard Solder vs. Material

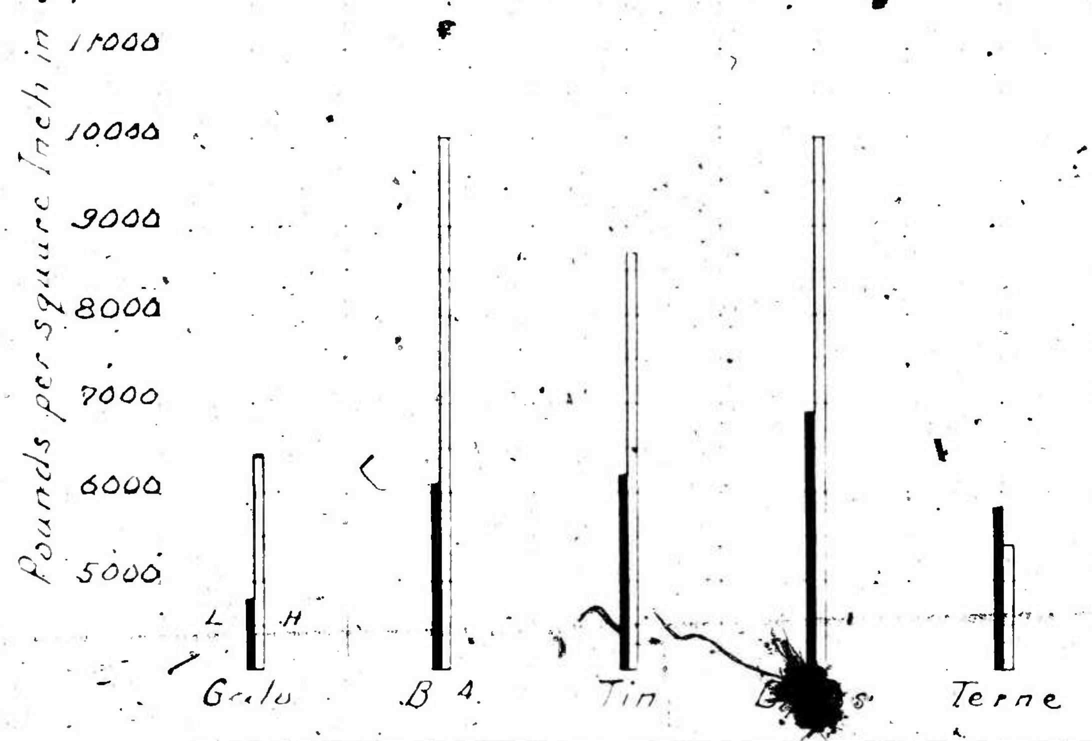
Fig. 6.



Tinless Solder

0 Percent Zinc vs. Material

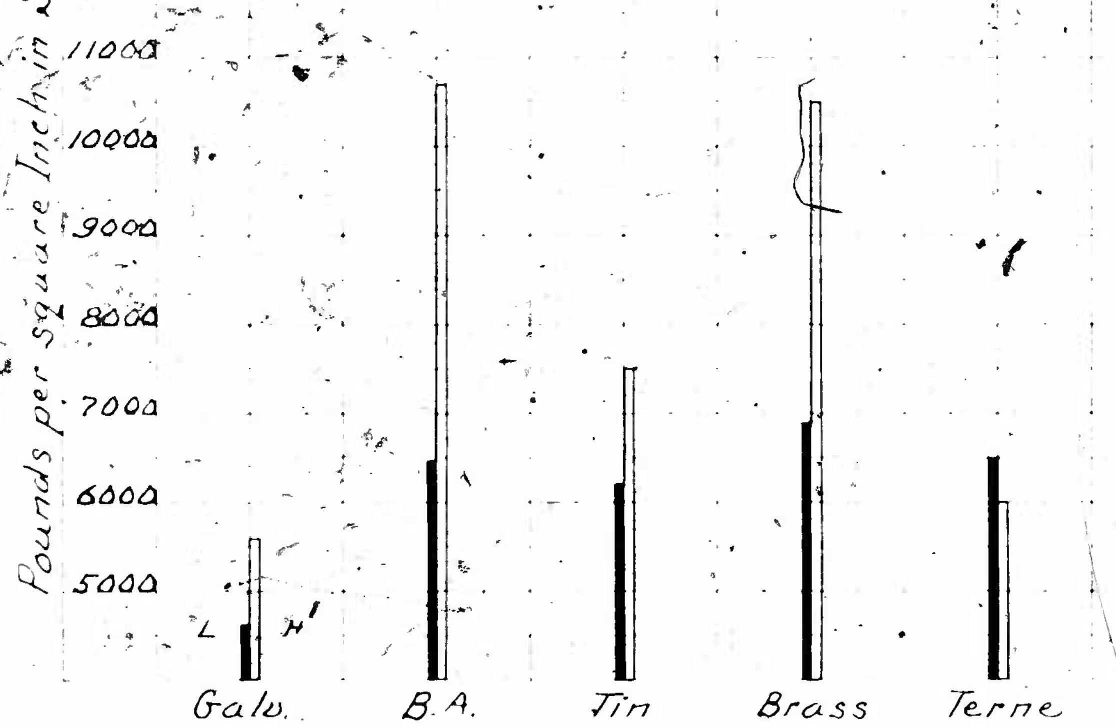
Fig. 7



Tinless Solder

1 Per Cent Zinc vs. Material

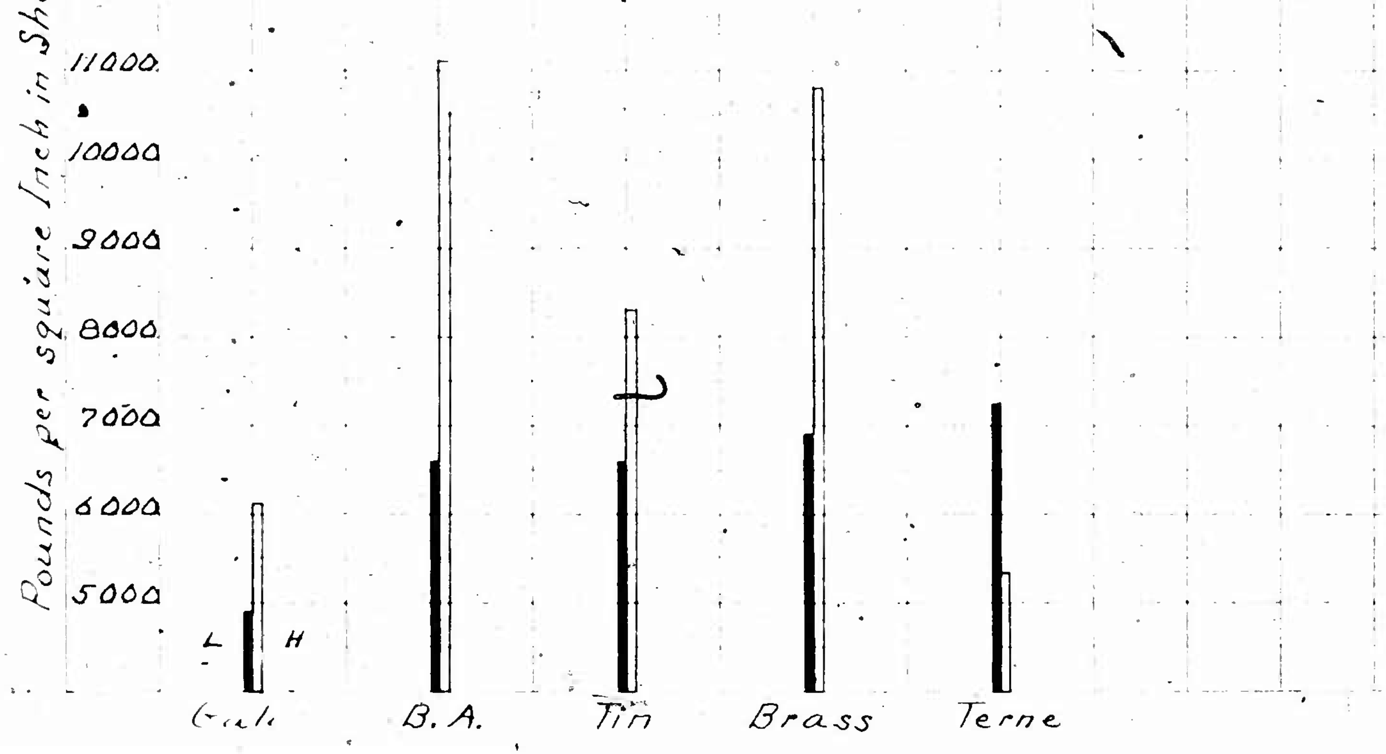
Fig. 8.



Tinless Solder

1.5 Per Cent Zinc vs. Material.

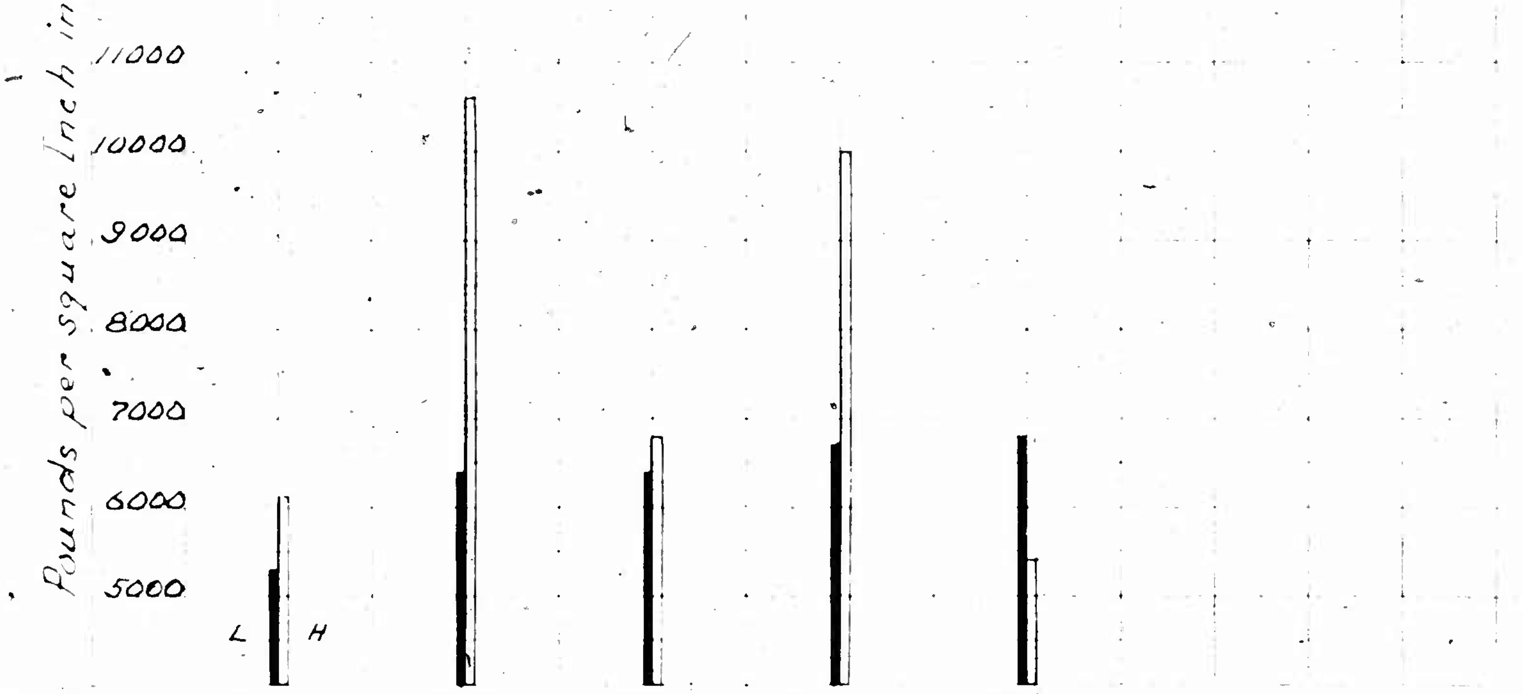
Fig. 9.



Tinless Solder

2 Per Cent Zinc vs Material

Fig. 10



Tinless Solder

4 Per Cent Zinc vs. Material

Fig. 11.